STATE OF ILLINOIS
DWIGHT H. GREEN, *Governor*
DEPARTMENT OF REGISTRATION AND EDUCATION
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DIVISION OF THE
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URBANA

REPORT OF INVESTIGATIONS — NO. 123

I. REACTION OF DIFFERENT CLAY MINERALS WITH SOME ORGANIC CATIONS

AND

II. REACTION OF CLAYS WITH ORGANIC CATIONS IN PRODUCING REFRACTORY INSULATION

BY

R. E. GRIM, W. H. ALLAWAY, AND F. L. CUTHBERT

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ORGANIZATION

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REACTION OF DIFFERENT CLAY MINERALS WITH SOME ORGANIC CATIONS*

BY

R. E. GRIM,† W. H. ALLAWAY,‡ AND F. L. CUTHBERT§

ABSTRACT

Selected pure samples of kaolinite, illite, and montmorillonite were washed with 0.05 N HCl until free from replaceable bases, washed with water or methanol, and then reacted with sufficient KOH to saturate the exchange complex with K^+ at pH 7. These K clays were given variable dosages of n-butylamine acetate, dodecylamine acetate, and ethyldimethyloctadecenylammonium bromide. The conclusions are as follows: (1) additions of amines or other organic cations in amounts less than equivalent to the base-exchange capacity of the clay are rather completely adsorbed in base-exchange reactions; amounts of large organic cations added in excess of the base-exchange capacity of the clay tend to be adsorbed by a different reaction, probably dependent on the action of the van der Waals' forces; and (2) the ability of clays to absorb water is greatly reduced by treating the clays with certain compounds that furnish a large organic cation.

INTRODUCTION

The data presented herein were obtained in the course of a fundamental study of bonding clays and molding sands.‖ Other reports of this cooperative research have been published elsewhere.[1]

Recent researches[2] have shown that the electrolyte content, including replaceable and soluble ions, is one of the factors controlling the properties of a clay material. Gieseking[3] and others,[4] furthermore, have shown that some organic cations may be held in a replaceable form by certain clay materials.

Part of the work on bonding clays involved a study of the influence of specific inorganic and organic cations on the bonding properties of various types of clay. This work included fundamental study of the reaction of the clay minerals with certain organic cations. An unexpected result was the development of a new method of producing lightweight clay products. The purpose of this report is to present the fundamental data. The method of making lightweight clay products is presented on page 15 of this report.

1(a) R. E. Grim and F. L. Cuthbert, "Some Clay-Water Properties of Certain Clay Minerals," *Jour. Amer. Ceram. Soc.*, 28 [3] 90–95 (1945); *Ill. State Geol. Survey Rept. Investigations*, No. 103 (1945).

(b) R. E. Grim and F. L. Cuthbert, "Bonding Action of Clays: I, Clays in Green Molding Sands," *Ill. State Geol. Survey Rept. Investigations*, No. 102, 55 pp. (1945); *Univ. of Ill. Eng. Expt. Sta. Bull.*, No. 357 (1945); *Ceram. Abs.*, 24 [10] 190 (1945).

(c) R. E. Grim and F. L. Cuthbert, "Bonding Action of Clays: II, Clays in Dry Molding Sands," *Ill. State Geol. Survey Rept. Investigations*, No. 110, 36 pp. (1946); *Univ. of Ill. Eng. Expt. Sta. Bull.*, No. 362 (1946); *Ceram. Abs.*, 29 [6] 108 (1946).

2R. E. Grim, "Modern Concepts of Clay Materials," *Jour. Geol.* 50 [3] 225–75 (1942); *Ill. State Geol. Survey Rept. Investigations*, No. 80 (1942); *Ceram. Abs.*, 21 [8] 177 (1942).

3J. E. Gieseking, "Mechanism of Cation Exchange in the Montmorillonite-Beidellite-Nontronite Type of Clay Minerals," *Soil Sci.*, 47 [1] 1–14 (1939); *Ceram. Abs.*, 18 [5] 136 (1939).

4S. B. Hendricks, "Base Exchange of the Clay Mineral Montmorillonite for Organic Cations and Its Dependence on Adsorption Due to van der Waals' Forces," *Jour. Phys. Chem.*, 45, 65–81 (1941); *Ceram. Abs.*, 21 [3] 68 (1942).

REVIEW OF LITERATURE

Other workers in this field have been primarily concerned with the reaction of organic cations, in relatively small dosages, with montmorillonite-type clays. Little or no information was available on the reaction of organic cations with clays of other mineralogical groups. Furthermore, the physical properties of clays treated with organic cations had not been the object of detailed study.

Gieseking[3] found that large organic cations were strongly adsorbed by clays of the montmorillonite type in exchange for H^+ ions. On the basis of X-ray diffraction patterns of clays treated with large organic cations, it appeared that these cations had assumed positions between the sheets of the layer lattice crystal units. It was also noted that montmorillonite clays, after treatment with large organic cations, did not exhibit the marked swelling and ready dispersibility which characterize the Na^+ saturated clays of this type.

Hendricks[4] found that organic cations were held to the surfaces of montmorillonite clays not only by Coulomb forces between the ions but also by van der Waals' attraction of the molecules to the surface. It was also demonstrated that the water content of amine salts of montmorillonite, in equilibrium with varying relative humidities, was less than that of the sodium and calcium salts of the same clay.

Recent work by Bradley[5] has indicated a stable association between montmorillonite clays and polyfunctional glycols, even though exchange of adsorbed cations was not evident. This work also indicated that certain amines were held to this clay mineral by forces in addition to the ionic-exchange charges. Hydrogen bonding between the aliphatic C atoms and the O ions of the silicate sheets is evidently operative in this situation.

Other evidences of specialized reactions between organic cations and clays include the observation[6] that characteristic colors are produced when montmorillonite clays are treated with certain aromatic amines. Van Baren[7] has also noted that the indices of refraction of soil clays were altered when the immersion liquid contained amino groups.

EXPERIMENTAL—MECHANISM OF REACTION

A set of experiments was conducted to determine whether or not organic cations were adsorbed in base-exchange reactions by clay of the kaolinite and illite types in a manner similar to that demonstrated by earlier workers for montmorillonitic clays. It also seemed desirable to determine whether amounts of the organic cation in excess of the base exchange capacity of the clay could be held in the clay.

The following clays were selected as examples of the various clay-mineral groups.

(1) *Kaolinite:* A kaolin from Bath, South Carolina.

(2) *Illite:* A fraction finer than 2 microns equivalent spherical diameter was isolated from an underclay of Pennsylvanian age, Grundy County, Illinois.

(3) *Montmorillonite:* Purified by removal of material coarser than 2 microns from Cretaceous bentonite, Monroe County, Mississippi.

Complete chemical and mineralogical data were available indicating that these materials were representative of their respective mineralogical groups.

The illite and montmorillonite clays were washed with $0.05N$ HCl until free of replaceable bases and then with water or methanol until free of chlorides. They were then dried and ground in an agate mortar. The kaolinite clay, as received, was found on analysis to be free of replaceable bases. The base-exchange capacities of the clays, determined by titrating the acid clays to pH 7.0 with KOH, were as follows:

[5]W. F. Bradley, "Molecular Associations Between Montmorillonite and Some Polyfunctional Organic Liquids," *Jour. Amer. Chem. Soc.*, 67 [6] 975–81 (1945); *Ill. Geol. Survey Rept. Investigations*, No. 108, 1945; *Ceram. Abs.*, 24 [10] 189 (1945).

[6]E. A. Hauser and M. B. Leggett, "Color Reactions Between Clays and Amines," *Jour. Amer. Chem. Soc.*, 62, 1911–18 (1940).

[7]F. A. Van Baren, "Influence of Different Fluids on Index of Refraction of Clay Minerals," *Z. Krist.*, 95, 464–69 (1936).

TABLE 1.—ADSORPTION OF ORGANIC CATIONS AND RELEASE OF EXCHANGEABLE POTASSIUM OF *n*-BUTYLA-
MINE ACETATE, DODECYLAMINE ACETATE, AND ETHYLDIMETHYLOCTADECENYLAMMONIUM BRO-
MIDE WITH KAOLINITE CLAY

No.	Clay (gm.)	Exchange-able K present (me.)	Organic electrolyte added (me.)	Vol. (cc.)	Organic cation absorbed (me.)	K released (me.)	pH	Bromide adsorbed
			n-Butylamine acetate					
1	50.0	1.0	0.5	400	0.32	0.24	6.6	
2	50.0	1.0	1.0	400	0.43	.36	6.7	
3	50.0	1.0	1.5	400	0.49	.45	7.1	
4	50.0	1.0	2.0	400	0.62	.48	7.2	
5	50.0	1.0	2.5	400	0.64	.54	7.2	
			Dodecylamine acetate					
6	50.0	1.0	0.5	400	0.47	.45	6.9	
7	50.0	1.0	1.0	400	0.93	.78	6.7	
8	50.0	1.0	1.5	400	1.26	.93	6.3	
9	50.0	1.0	2.0	400	1.43	.96	5.7	
10	50.0	1.0	2.5	400	1.74	.96	5.6	
			Ethyldimethyloctadecenylammonium bromide					
11	50.0	1.0	0.5	400	0.47	.40	7.0	0.09
12	50.0	1.0	1.0	400	0.92	.76	6.9	.06
13	50.0	1.0	1.5	400	1.41	.92	6.8	.36
14	50.0	1.0	2.0	400	1.91	.96	6.8	.77
15	50.0	1.0	2.5	400	2.41		6.7	

TABLE 2.—ADSORPTION OF ORGANIC CATIONS AND RELEASE OF EXCHANGEABLE POTASSIUM IN REACTION OF
n-BUTYLAMINE ACETATE, AND DODECYLAMINE ACETATE WITH ILLITE CLAY

No.	Clay (gm.)	Exchange-able K present (me.)	Organic electrolyte added (me.)	Vol. (cc.)	Organic cation adsorbed (me.)	K released (me.)	pH
			n-Butylamine acetate				
1	8.51	2.0	1.0	250	0.64	0.64	7.45
2	8.51	2.0	2.0	250	1.12	1.05	7.3
3	8.51	2.0	3.0	250	1.30	1.29	7.35
4	8.51	2.0	4.0	250	1.60	1.30	7.45
5	8.51	2.0	5.0	250	1.82	1.37	7.5
			Dodecylamine acetate				
1	8.51	2.0	1.0	250	0.98	1.07	7.6
2	8.51	2.0	2.0	250	1.90	1.72	6.0
3	8.51	2.0	3.0	250	2.63	1.79	5.7
4	8.51	2.0	4.0	250	3.26	1.81	5.6
5	8.51	2.0	5.0	250	4.16	1.83	5.6

montmorillonite, 72 me. per 100 gm.; illite, 23 me. per 100 gm., and kaolinite, 2 me. per 100 gm. Base-exchange capacities of these same clays were slightly higher than these values when determined with Ca^{++} as the saturating ion.

The following procedure was used in studying the reaction of the K-saturated clays with *n*-butylamine acetate, dodecylamine acetate, and ethyldimethylocta-decenylammonium bromide. Samples of the acid clays were suspended in water, and

Table 3.—Adsorption of Organic Cations and Release of Exchangeable Potassium in Reaction of *n*-Butylamine Acetate, Dodecylamine Acetate, and Ethyldimethyloctadecenylammonium Bromide with Montmorillonite Clay

No.	Clay (gm.)	Exchangeable K present (me.)	Organic electrolyte added (me.)	Vol. (cc.)	Organic cation absorbed (me.)	K released (me.)	pH	Bromide adsorbed
				n-Butylamine acetate				
1	2.78	2.0	1.0	250	0.82	0.52	7.7	
2	2.78	2.0	1.5	250	1.05	0.91	7.5	
3	2.78	2.0	2.0	250	1.29	1.25	7.4	
4	2.78	2.0	2.5	250	1.42	1.38	7.6	
5	2.78	2.0	3.0	250	1.60	1.47	7.6	
6	2.78	2.0	4.0	250	1.65	1.51	7.6	
7	2.78	2.0	5.0	250	1.73	1.50	7.4	
				Dodecylamine acetate				
1	2.78	2.0	0.5	250	0.45	0.55	6.8	
2	2.78	2.0	1.0	250	1.00	1.05	7.0	
3	2.78	2.0	1.5	250	1.50	1.48	6.6	
4	2.78	2.0	2.0	250	1.85	1.72	5.9	
5	2.78	2.0	2.5	250	2.25	1.86	5.7	
6	2.78	2.0	3.0	250	2.50	1.78	5.6	
7	2.78	2.0	4.0	250	3.00	1.76	5.6	
8	2.78	2.0	5.0	250	3.50	1.76	5.6	
				Ethyldimethyloctadecenylammonium bromide				
1	2.78	2.0	1.0	250	1.00	0.94	7.0	0.06
2	2.78	2.0	2.0	250	2.00	1.66	6.7	0.21
3	2.78	2.0	3.0	250	2.94	1.90	6.5	1.02
4	2.78	2.0	4.0	250	3.94	1.90		1.97
5	2.78	2.0	5.0	250	4.46	1.98	6.2	2.32

sufficient KOH was added to saturate the exchange complex with K^+ at pH 7.0. After shaking intermittently for about 48 hours, varied dosages of the three organic electrolytes were added to the several flasks, and the volume of the systems was adjusted to 250 or 400 cc. After intermittent shaking for 48 hours, the liquid phase of the system was removed and aliquots were analyzed for N and K and the pH was determined. Where the organic bromide was added to the clay systems, bromide determinations were also made on aliquots of the liquid phase. The amounts of the organic cation adsorbed and of the K released were then calculated.

The composition of the systems and the results of the experiment are shown in tables 1, 2, and 3. It should be noted that the systems containing kaolinite were less concentrated in terms of replaceable K than were the montmorillonite and illite systems.

This was necessary because of the low base-exchange capacity of the kaolinite clay. Kaolinite systems at the concentration used in the other clays would not have been sufficiently fluid to permit thorough mixing by the shaking procedure.

DISCUSSION OF RESULTS

Figures 1, 2, and 3 illustrate the relation between the organic cation adsorbed and the K released in the kaolinite, illite, and montmorillonite systems.

The difference in the manner in which each of the three organic electrolytes reacted with the clays is apparent from the graphs. *n*-Butylamine ions, with the smallest molecular size of the three organic bases, was not adsorbed in amounts greater than the base-exchange capacity by any clay. The amount of K released to the solution closely paralleled that of the *n*-butylamine ions

Fig. 1.—Amounts of organic cation adsorbed and K released by kaolinite clay on treatment with *n*-butylamine acetate, dodecylamine acetate, and ethyldimethyloctadecenylammonium bromide; 50 gm. of kaolinite containing 1.0 me. replaceable K plus increments of organic electrolyte in 400-cc volume.

Fig. 2.—Amounts of organic cation adsorbed and K released by illite clay on treatment with *n*-butylamine acetate and dodecylamine acetate; 8.50 gm. illite clay containing 2.0 me. of replaceable K plus increments of organic electrolyte in 250-cc. volume.
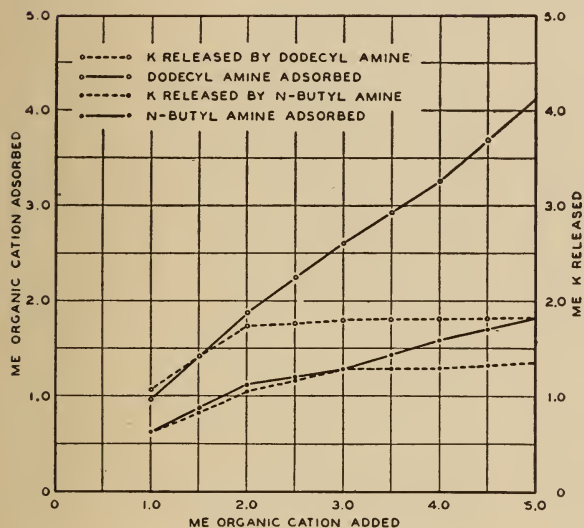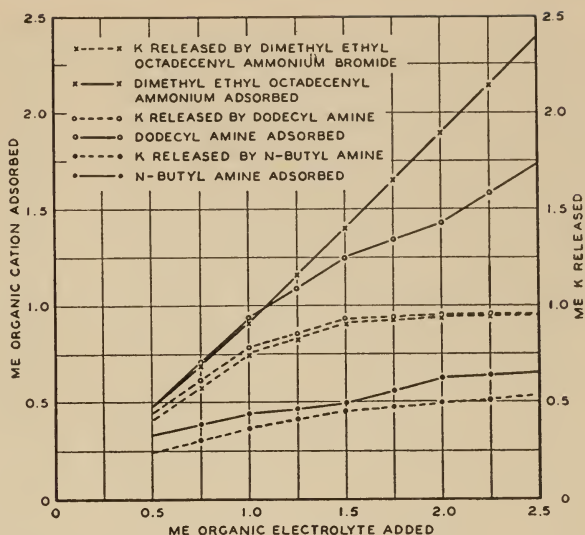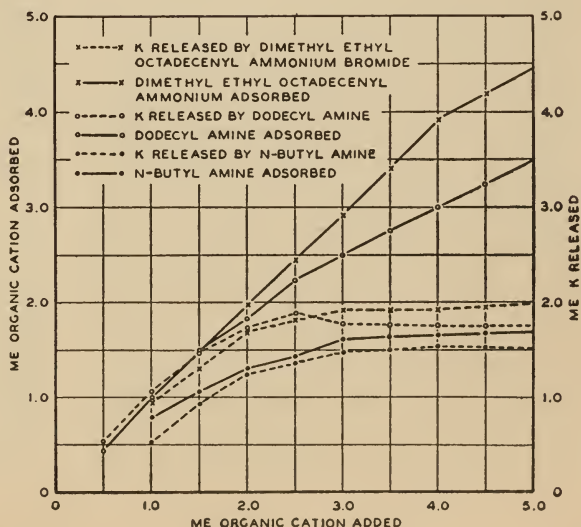

Fig. 3.—Amounts of organic cation adsorbed and K released by montmorillonite clay on treatment with *n*-butylamine acetate, dodecylamine acetate and ethyldimethyloctadecenylammonium bromide; 2.78 gm. of montmorillonite clay containing 2.0 me. of replaceable K plus increments of organic electrolyte in 250-cc. volume.

adsorbed, indicating that nearly all of this amine was adsorbed in a base-exchange reaction. On the other hand, both dodecylamine and ethyldimethyloctadecenylammonium ions were readily adsorbed in excess of the base-exchange capacity, after nearly all of the replaceable K had been removed from the clay. It seems probable, therefore, that adsorption of these materials took place due to two separate processes. When the amount of dodecylamine or ethyldimethyloctadecenylammonium ions added to the clay system was equal to or less than the replaceable potassium present, the organic cation was adsorbed and the potassium was released by the clay in a base-exchange reaction. Larger additions of the organic cation were adsorbed in part by this exchange reaction and in part by another type of adsorption which was proably due to van der Waals' forces. This is in accord with the work of Hendricks,[4] who found such forces to be operative under similar conditions. It will also be noted that the ethyldimethyloctadecenylammonium ion was more strongly adsorbed than the dodecylamine. This is to be expected since the van der Waals' forces would be stronger for the larger ion. The base-exchange adsorption was apparently the most stable of the two types of adsorption.

The question immediately arises as to whether the organic cations that were adsorbed in excess of the base-exchange capacity were held as ions or as undissociated molecules of the organic electrolyte. The data on bromide adsorption indicate that in the case of the ethyldimethyloctadecenylammonium bromide, practically all adsorption in excess of the base-exchange capacity was due to adsorption of undissociated molecules. The pH values of the systems never got below 6.2, which was the pH of the ethyldimethyloctadecenylammonium bromide solution at the same dilution. If the cation from this electrolyte had been adsorbed separately from the anion and no other cation were removed from the clay in the process, the pH of the systems would have been much lower because of the HBr remaining in solution. On the other hand, in the systems containing dodecylamine ace-

tate, the pH dropped to about 5.6 when amounts of the amine in excess of the exchange capacity were adsorbed. As the dodecylamine acetate solution was about pH 7.0, it seems quite possible that this low pH was due to acetic acid remaining in the solution following ionic adsorption of the cation of this electrolyte. Since no data on the adsorption of acetate ions were obtained, it is possible that ionic and molecular adsorption were both active in holding amounts of the amine in excess of the base-exchange capacity.

Varied effects of the three organic electrolytes on the degree of dispersion of the clays in distilled water were noted. The potassium-saturated clays were highly dispersed, especially the montmorillonite and illite. Small additions of any of the three organic compounds flocculated the clay. The flocculated clays exhibited a feathery appearance and large settling volume. In the case of *n*-butylamine acetate and dodecylamine acetate, no redispersion of the clays was noted at the higher dosages. When ethyldimethyloctadecenylammonium bromide, however, was added to the montmorillonite clay at twice the base-exchange capacity, a certain amount of clay remained in suspension; and, at a dosage of two and one-half times the base-exchange capacity, the clay was highly dispersed. It seems that this dispersion of the clay at high dosages of the organic bromide may have been due to a random adsorption of organic bromide molecules. The hydrophyllic part of such molecules in some cases would be on the surface and would attract water to this surface, thus preventing the flocculation of the clay.

Effect of Organic Cations on Water Relationships of Clays

The adsorption of large organic cations in amounts equivalent to or greater than the base-exchange capacity of clays would alter, to a marked degree, the nature of the surfaces of the clay particles and would affect those properties which depend on surface reactions. In view of the results shown in the section, *Discussion of Results*, it

TABLE 4.—WATER CONTENT OF KAOLINITE AND MONTMORILLONITE CLAY AS AFFECTED BY RELATIVE HUMIIDTY AND ORGANIC ELECTROLYTE TREATMENT

Clay	Treatment	Relative humidity 52%		98%	
		1 BX*	2 BX*	1 BX*	2 BX*
Montmorillonite	Untreated acid clay	16.0		42.2	
"	n-Butylamine acetate	7.1	4.9	17.9	27.7
"	Dodecylamine acetate	3.1	4.4	12.1	12.5
"	Ethyldimethyloctadecenylammonium bromide	3.6	3.6	23.4	25.9
Kaolinite	Untreated acid clay	0.6		5.4	
"	n-Butylamine acetate	0.5	0.5	5.2	3.9
"	Dodecylamine acetate	0.4	0.3	2.9	2.1
"	Ethyldimethyloctadecenylammonium bromide	0.5	0.4	3.2	3.8

*Organic electrolyte added in quantities equal to one times and two times the base-exchange capacity, respectively.

seemed desirable to determine, under various conditions, the water content of clays treated with large amounts of organic electrolytes. Accordingly, montmorillonite and kaolinite clays were each treated with n-butylamine acetate, dodecylamine acetate, and ethyldimethyloctadecenylammonium bromide. The acid clays were treated with solutions of the organic electrolytes at concentrations equivalent to one and two times the base-exchange capacity of the clay. The mixtures were then dried on a steam bath and the clays were reground. The clays were then spread in thin layers in shallow aluminum pans and kept for three weeks in closed containers where relative humidities of 52% and 98% were maintained. The 52% relative humidity was obtained by placing a saturated solution of $Mg(NO_3)_2$ in part of the container. The 98% relative humidity was obtained by placing a saturated solution of $CaSO_4$ in part of the container, and the containers were held at 25°C. The results are shown in table 4.

It is evident that the ability of the clays to absorb water was markedly lowered by the treatment with organic electrolytes. The decrease in water content as compared with that of the untreated acid clay was relatively greater for montmorillonite than for kaolinite, which would indicate that the adsorbed ions on montmorillonite occupy a greater proportion of the surface of the clay than do the adsorbed cations on kaolinite. This would be in agreement with the modern ideas of the structures of these two clay minerals.

The water content of clays treated with dodecylamine acetate was generally lower than that obtained by treatment with either n-butylamine or ethyldimethyloctadecenylammonium bromide. This was particularly true at 98% relative humidity. No great change in water content was obtained by increasing the dosage of organic electrolyte treatment from one to two times the equivalent of the base-exchange capacity.

Hendricks[4] pointed out that the montmorillonite salts of organic cations adsorb less water than metallic ion salts of the same clays because of two factors, namely, (1) the large volumes of the cations employed exclude water from large areas of the surfaces concerned and (2) the structure of the hexagonal network of water molecules on the remainder of the clay surface would be destroyed because of the shape of the organic cations adsorbed.

SUMMARY

Certain fundamental and practical aspects of the use of amines and other organic cations in the production of lightweight-insulating refractories were investigated.

This study may be summarized as follows:

1. Additions of amines or other organic cations in amounts less than equivalent to the base-exchange capacity of the clay are rather completely adsorbed in base-exchange reactions. Amounts of large organic cations added in excess of the base-exchange capacity of the clay tend to be adsorbed by a different reaction, probably dependent on the action of van der Waals' forces.

2. The ability of clays to absorb water is greatly reduced by treating the clays with certain compounds that furnish a large organic cation.

REACTION OF CLAYS WITH ORGANIC CATIONS IN PRODUCING REFRACTORY INSULATION*

BY

R. E. GRIM, W. H. ALLAWAY, AND F. L. CUTHBERT†

ABSTRACT

Slips prepared in certain ways with some organic compounds shrink only slightly after casting so that their shape and porosity are not lost on drying or later firing. This provides a possible method of producing refractory insulation without final sawing to shape. The compounds effective in producing such porous clay bodies are certain amines or other organic cations, in which one or more large hydrocarbon groups are attached to the basic nitrogen atom. The results of studies concerned with molding and other problems connected with production of insulating refractories by this process are given.

INTRODUCTION

Early in the course of investigations‡ on the reaction of clay with organic cations,[1] it was noted that whenever a suspension of clay, treated with certain organic compounds (mostly amines or their salts) was dried or filtered, the clay residue was quite porous. Apparently the clay particles did not orient themselves into a dense mass on drying. It was discovered also that slips prepared in certain ways with dodecylamine acetate or other somewhat similar compounds shrank only slightly after casting so that their cast shape and porosity were not lost on drying or on later firing.

It seemed possible that this fact could be made the basis of a simple process for producing porous insulating refractories which might obviate the need for sawing to shape after drying.

PROCEDURE

A survey was conducted to determine what compounds were effective in producing porous clay bodies that were stable on drying and firing. An underclay of Pennsylvanian age from Grundy County, Illinois, was used for this work. This clay was predominately composed of kaolinite, and its base-exchange capacity was about 11 me. per 100 gm. A 1.0% solution of the various organic compounds under investigation was prepared, and the clay was added to these solutions. The solution was mixed with a high-speed mixer during the time the clay was being added, and mixing was continued until no further increase in the volume of the mixture was noticed. Ordinarily 1000 gm. of clay were added to 1000 cc. of the 1.0% solution of the organic compound, but 500 gm. of clay and 500 cc. of solution were used in a few cases. Since the exchange capacity of the clay was 11 me. per 100 gm., there would be 11 me. of exchange capacity for each gram of the organic compound present. Therefore, organic amines with an equivalent weight of less than 99 would have been added to the clay in amounts greater than the base-exchange capacity, and heavier organic cations would have been added in amounts less than equivalent to the base-exchange capacity.

After thorough mixing or beating of the clay and the organic solution, the mixture was poured into oiled enamel pans, about 6 in. wide, 9 in. long, and 2 in. deep; it was dried by placing it on a steam radiator and

then cut into blocks. The bulk densities of the blocks were determined and their pore structure was studied.

Discussion of Test Results

Marked differences in the effect of the organic compounds on the properties of the slip and on the pieces dried from it were immediately evident. Large amine and other nitrogenous organic cations were found to produce clay slips which could be beaten into a stiff voluminous mass. Pieces dried from these slips were very light, usually having a bulk density of less than 1 (62 lb. per cu. ft.), and they contained small pores uniformly distributed throughout the dried pieces.

Amines of relatively low molecular weight and divalent amines or organic bases did not produce slips that could be dried to form uniform lightweight blocks. No organic cation without at least one 4-carbon aliphatic chain or one 6-carbon ring was effective in producing the desired structure in the dried blocks. Hydroxy amines were ineffective in this process.

A list of some of the compounds, which produced test pieces of low bulk density and with uniformly distributed fine pores, is as follows:

(1) Dodecylamine acetate
(2) Tri-*n*-butylamine
(3) β-naphthylamine acetate
(4) *p*-Toluidine acetate
(5) Phenylhydrazine
(6) *n*-Hexylamine
(7) Di-*n*-butylamine
(8) Aniline
(9) Benzylamine
(10) Tetra-*n*-butylammonium iodide
(11) *n*-Amylamine
(12) Dibenzylamine acetate
(13) *n*-Butylamine acetate
(14) Benzyldodecyldimethylammonium chloride
(15) Dodecyldimethylamine sulfate
(16) Ethyldimethyloctadecenylammonium bromide
(17) Mixed octadecyl- and hexadecylamine acetates
(18) Several cationic wetting agents of uncertain composition

The following compounds were investigated, but they did not produce test pieces with low bulk density:

(1) Dimethylamine
(2) Trimethylamine
(3) Diethylamine
(4) Tetraethylammonium chloride
(5) Pyridine
(6) Piperidine
(7) 2, 4, 6-collidine
(8) Triethanolamine
(9) β-hydroxyethyl-*p*-toluidine
(10) Benzidine hydrochloride
(11) *o*- and *m*-phenylenediamines
(12) *o*-Tolidine
(13) Ethylenediamine

Many of the compounds found to be effective in producing clay slips which could be dried to form porous test pieces were those that are commonly used as cationic wetting or frothing agents. It seemed that their effect in producing porous clay bodies might be due to the fact that a foam was formed during the mixing of the slip. If this were true, it seemed likely that anionic wetting agents, such as aliphatic acids, might have the same effect. A number of common anionic wetting agents were therefore included in the survey. Although slips containing anionic wetting agents could be mixed or beaten until a voluminous foamy slip was obtained, it was found that such slips soon collapsed, and test pieces dried from them were very dense and frequently were badly cracked.

On the basis of the chemical nature of the compounds effective in producing porous clay pieces and in view of the effect of some of these compounds on the water adsorption by clays, a hypothesis of the mechanism of the formation of porous test pieces can be evolved.

An examination of the list of compounds effective in producing the desirable porous structure reveals certain molecular structure characteristics to be common to all of them. All of these compounds would furnish a monovalent organic cation, having one or more hydrocarbon radicals of relatively large size. Furthermore, no groups are present, such as OH, SO_3, or others, that might be expected to make the molecules more hydrophyllic. In view of the results on the nature of the reaction of such cations with the different clay minerals, it would be expected that the organic cation would be taken up by the clay in a base-exchange

reaction. The basic nitrogen atom of the molecule would be closely held to the mineral surface, and the hydrocarbon part of the molecule would be arrayed on the surface or directed outward from the surface. This would lead to the formation of considerable areas on the mineral that would not be wetted by water. The effects of treating kaolinite and montmorillonite with various amines on the water adsorption by these clays are in agreement with this hypothesis.

When the slip containing clay with some nonwettable surfaces is mixed with a high-speed mixer, air is incorporated into it. This air is then held in small bubbles on the nonwettable surfaces of the clay. Continued adsorption of air by the clay in this manner leads to a marked increase in the volume of the slip, and the slip tends to become stiffer or less fluid because the air is rigidly held to the clay particles and adds to the volume of the solid phase.

When such a slip is dried, the air does not escape because it is held to the solid phase rather than being incorporated into the liquid phase. The clay particles, moreover, do not become oriented into their most dense arrangement because the air bubbles and nonwettable surfaces of the clay disrupt the continuity of the water films on the clay surfaces and prohibit the water from functioning as a lubricant in permitting the clay to come to an oriented arrangement. As a consequence, particularly of the random arrangement of the clay particles and their nonwetted characteristic, the mass of clay, water, and air has a certain structure which does not collapse when the water is removed. The clay body resulting from the drying of such slips therefore has low bulk density.

Laboratory Production of Light-weight Brick by Treating Clays with Dodecylamine Acetate

Although many organic compounds were successfully used in the production of small-sized porous blocks, any compound that would be suitable for the practical production of such blocks must meet certain requirements as to cost and ease of handling. Following the consideration of a number of amines and other compounds containing a suitable organic cation, it was decided to use dodecylamine acetate for most of the further development work. This compound was low in cost, readily soluble in water, and, as shown formerly, was effective in preventing water adsorption by clays. Other compounds that were given consideration and showed promise in large-scale work included some of the toluidines and certain cationic wetting agents.

PROCESSING OF SLIP

The ratio of dodecylamine acetate to clay was studied in slips containing equal weights of clay and water. The clay was the same kaolinitic Pennsylvanian under-clay used in the survey of effective compounds. This clay was treated with 0.5, 1.0, 2.0, 3.0, and 5.0% of its weight of dodecylamine acetate, which is equal to approximately 20, 40, 80, 120, and 200% of saturation of its exchange capacity. It was found that increasing the dosage of dodecylamine-acetate treatment above 1% by weight of the clay did not decrease the bulk density of the blocks. Furthermore, the pieces prepared from the slips treated with the higher percentages were very weak and, when dry, they tended to "powder off" and crumble very easily. This tendency to crumble can be readily explained on the basis of the work of Grim and Cuthbert,[2] who found that the development of bonding strength in clay bodies is contingent upon the formation of films of water on the surfaces of the individual particles. Such films could not be continuous upon clays containing adsorbed dodecylamine.

The fact that the dried pieces were quite weak and required careful handling until fired to develop vitreous bonds led to an investigation of the procedures for imparting greater strength to the unfired pieces. Wyoming bentonite was used, but the extreme drying shrinkage of this clay caused

[2]R. E. Grim and F. L. Cuthbert, "Some Clay-Water Properties of Certain Clay Minerals," *Jour. Amer. Ceram. Soc.* 28 [3] 90–95 (1945); *Ill. State Geol. Survey Rept. Investigations,* No. 103 (1945).

the pieces to crack. Sodium silicate, calcium sulfate, and Lumnite cement were also studied, but the fusion point of the finished product was lowered by these materials. Corn flour was used with considerable success, and pieces prepared by adding about $\frac{1}{2}\%$ corn flour to the clay before mixing the slip were strong enough to be readily handled in the unfired condition.

Another point considered was the ratio of clay to water in the slip. It was found that the water content of the slip must be high enough to render the slip sufficiently fluid to permit air to be mixed into it and to permit formation of small bubbles from the incorporated air. At the same time, excessive water content would increase drying costs as well as the drying shrinkage. The selection of the clay-water ratio in the slip therefore must represent a balancing of these two effects.

A clay-to-water ratio of about 10 to 9 was found necessary to permit the incorporation of sufficient air into the slips to produce blocks with bulk densities approaching those of commercially available insulating refractories. The drying shrinkage of such slips was not excessive.

The use of some grog in the slips was effective in bringing about a slight reduction in amount of water necessary to produce fluid slips. The drying shrinkage of such slips was also lower than that of slips containing no grog. When grog, prepared by calcining a highly refractory white halloysite clay, was added in the amount of 25% of the solid material used, the fusion point of the blocks was raised.

FORMING AND DRYING

The molding and drying methods for the preparation of blocks equal in size to standard brick presented certain obstacles. Although the water content of the slips at pouring time was quite high, the drying shrinkage was not nearly so great as would be expected from the drying shrinkage of similar slips without amine treatment. It was necessary, however, to dry the material quite slowly to prevent cracking. Plaster molds were found to be unsatisfactory be-

cause the water was removed from the slip so rapidly that cracks developed and the pieces did not break free from the plaster molds properly. Enameled pans, about 5 by 10 in. in size and $3\frac{1}{2}$ in. deep and oiled with light oil, were satisfactory as molds. The drying shrinkage of the pieces was not the same in all directions; a slight amount of settling apparently contributed to greater vertical shrinkage. Fired pieces prepared in such molds were slightly larger than standard 9-in. brick.

The slips were dried by directing 500-watt infrared heat lamps toward the surfaces of the molds from a distance of about 12 in. This procedure resulted in satisfactory drying and very few pieces developed cracks in the drying process. Molds containing 1800 gm. of clay and 1700 gm. of water were dried to a condition suitable for firing in kilns in about 15 hours. Other drying procedures could probably be used if the drying rate was slow enough and if the bottoms of the molds did not become excessively heated until most of the water had been driven off.

The drying shrinkage of these slips was quite low and very uniform. It seems quite possible that, with properly designed molds, standard shapes could be produced without any trimming of the fired materials.

PROPERTIES OF REFRACTORY PRODUCTS

The brick, prepared by the methods outlined, had properties such as thermal conductivity, bulk density, and reheat shrinkage comparable with those of commercial products of the same heat-duty class. Figure 1 shows the thermal conductivity of blocks prepared from slips containing 900 gm. of Pennsylvanian underclay, 10 gm. of dodecylamine acetate, 5 gm. of corn flour, and 850 cc. of water.

The commercial production of lightweight-insulating refractories by this process appears to be possible and to have certain advantages. The cost of the amine treatment would be low—not greatly in excess of the cost of combustible materials, such as are commonly used at the present time in preparation of these materials.
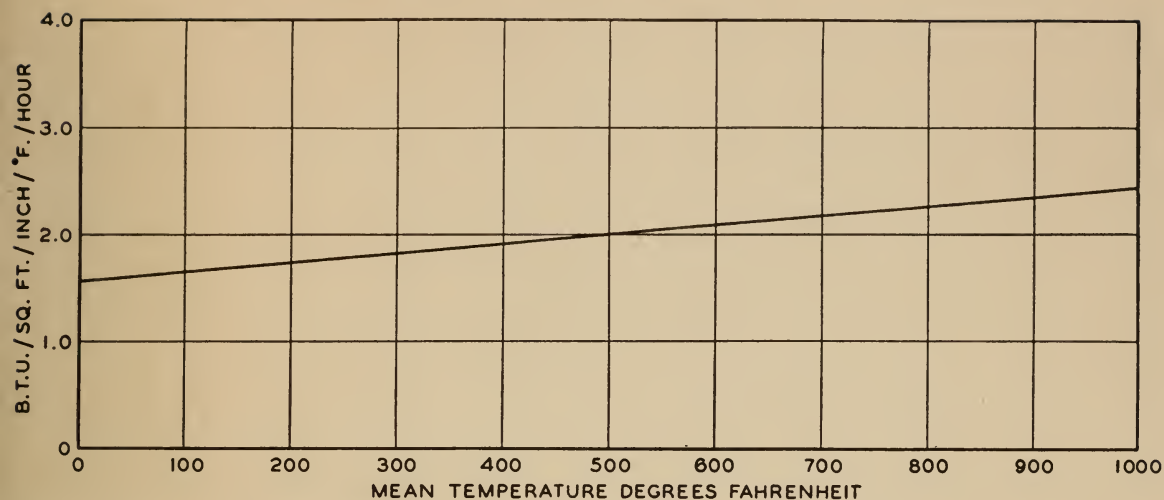
FIG. 1.—Thermal conductivity of brick with a density of 46 lb. per sq. ft. produced by process described.

Furthermore, the firing difficulties that are often encountered when a combustible material is used to impart porosity to ceramic insulators are avoided. The amount of gases formed in the firing of blocks rendered porous by amine treatment is so low that no tendency for rupture or blows is encountered. If trimming of the fired or unfired blocks can be avoided through proper selection of molds, a marked advantage over processes now in common use would be obtained. It might also be possible to smooth the surface before firing so that a surface seal could be developed.

Some of the disadvantages of the method are (1) a close control over the selection of raw materials and mixing and molding is required; (2) unusual molding methods are required and a large amount of water must be volatilized in the drying process; and (3) the dried but unfired pieces are not rugged and require careful handling from the drier to the kiln and some support in the kiln.

SUMMARY

1. Porous clay bodies, capable of being fired without losing their porous nature or shape, can be prepared by mixing air into fluid clay slips that contain compounds which furnish a large organic cation.

2. The compounds effective in producing porous clay bodies by this process are amines or other organic cations in which one or more large hydrocarbon groups are attached to the basic nitrogen atom.

3. A possible mechanism is outlined for producing porous clay bodies by treatment of the clay with organic cations.

4. The results of studies concerned with the molding and other problems connected with production of insulating refractories by this process are given. It seems quite possible that the reaction of clays with certain organic cations can be utilized in the commercial production of insulating refractories.